

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
25 April 2002 (25.04.2002)

PCT

(10) International Publication Number
WO 02/32227 A1

(51) International Patent Classification⁷: **A01N 57/20**,
25/02, 25/30

John, David [AU/AU]; 6 Burwood Court, Thomastown,
VIC 3074 (AU).

(21) International Application Number: PCT/AU01/01310

(74) Agent: **ALLENS ARTHUR ROBINSON PATENT & TRADE MARKS ATTORNEYS**; 530 Collins Street, Melbourne, VIC 3000 (AU).

(22) International Filing Date: 17 October 2001 (17.10.2001)

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(25) Filing Language: English

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(26) Publication Language: English

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(71) Applicant (for all designated States except US): **VICTORIAN CHEMICALS INTERNATIONAL PTY LTD** [AU/AU]; 37-49 Appleton Street, Richmond, VIC 3121 (AU).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **KILLICK, Robert, William** [AU/AU]; 14 Dallas Street, Mount Waverley, VIC 3149 (AU). **KILLICK, Andrew, Robert** [AU/AU]; 10 Park Street, Richmond, VIC 3121 (AU). **JONES, Peter, William** [AU/AU]; 65 Menzies Road, Menzies Creek, VIC 3159 (AU). **WRIGLEY, Peter, Ronald** [AU/AU]; 6 Handel Court, Blackburn, VIC 3130 (AU). **MORRISON,**



WO 02/32227 A1

(54) Title: HERBICIDE COMPOSITION

(57) **Abstract:** There is provided an essentially non-aqueous homogeneous liquid herbicide composition comprising: a) a lipophilic solvent soluble complex comprising the reaction product of: i) not in excess of about 35 % by weight of one or more lipophobic herbicides having an acidic moiety; and ii) not in excess of about 99 % by weight of one or more tertiary dimethylamines of the structure $(\text{CH}_3)_2\text{N}-\text{R}$ wherein R contains an alkyl group of at least 8 carbon atoms and may contain other chemical moieties and wherein is at least one mole equivalent of such amine to eachmole of lipophobic herbicide; b) not in excess of about 60 % by weight of one or more essentially non-aqueous polar solvents having low volatility; c) not in excess of about 90 % by weight of one or more additional solvents selected from the group consisting of low to medium HLB surfactants; and d) not in excess of about 99 % by weight of one or more lipophilic carriers.

Herbicide Composition

Field of the invention

The invention relates to herbicide compositions. More particularly, the invention relates to essentially non-aqueous homogeneous herbicide compositions comprising lipophilic
5 solvent soluble complexes for application without dilution in water.

Background of the invention

In this specification, where a document, act or item of knowledge is referred to or discussed, this reference or discussion is not to be taken as an admission that the document, act or item of knowledge or any combination thereof was at the priority date:

- 10 (a) part of common general knowledge; or
(b) known to be relevant to an attempt to solve any problem with which this specification is concerned.

A herbicide composition typically has to be in a form from which it is available to act upon the target. If, for example, a herbicide composition is sprayed on a plant and the carrier
15 evaporates, the herbicide can be left solid and essentially unavailable for uptake.

Whilst the following discussion concerns glyphosate, it is to be understood that the same principles apply to all lipophobic herbicides having an acidic moiety.

Glyphosate is a non-selective herbicide which is applied in aqueous solutions to control weeds in agricultural, industrial and domestic situations. There has also been development
20 of crops which are resistant to herbicides, such as glyphosate and glufosinate, so that the herbicides may be used post emergent to protect the crop. In this specification, the term “glyphosate” refers to N-(phosphonomethyl)glycine CAS No. [1071-83-6]. Currently, glyphosate is neutralised by a base, such as isopropylamine, to allow it to be carried in an aqueous system.

25 Adjuvants are commonly used with these aqueous glyphosate compositions to improve the efficacy or induce other desirable properties. Adjuvants can be either formulated into commercial ready-to-use glyphosate-containing products or sold as additives to be added to the tank mix. These adjuvant materials include (i) surfactants and/or oils for wetting,

spreading and spray retention, (ii) buffering agents and water conditioners for protecting the glyphosate and (iii) polymeric materials which may reduce spray drift.

Sometimes the adjuvant is lipophilic, such as petroleum oils, vegetable oils or esterified oils, and, in these circumstances, an emulsifying system is also typically necessary to
5 enable the hydrophobic adjuvant to form an emulsion with the aqueous glyphosate composition. When used with lipophilic adjuvants and/or oil carriers, the glyphosate is expected to remain in the aqueous phase and may not fully benefit from the use of such a lipophilic adjuvant.

There have been attempts to improve the efficiency of glyphosate which include the use of
10 higher molecular weight amines to form a salt with the glyphosate. However, most of these attempts with salts of higher molecular weight amines were focussed on the conventional glyphosate application system wherein the product is diluted in water for use. The amines which are described in these attempts include primary, secondary and tertiary amines.

15 The authors are aware of only one attempt to form essentially non-aqueous compositions of herbicides and these compositions were intended for application by electrostatic spraying. This attempt teaches the preferred use of a stoichiometric amount of a primary alkyl amine having 13 to 17 carbon atoms to form a salt with the herbicide. It also teaches the use of a significant portion of a volatile polar solvent in the formation of the salt and the
20 composition which is applied.

Current spray application technology enables the application of essentially non-aqueous agrochemical compositions as well as aqueous compositions. Oil-soluble (lipophilic) insecticides and herbicides can be diluted in lipophilic carriers, such as petroleum or vegetable-based oils for spraying rather than dilution in water. By choosing appropriate
25 lipophilic carriers, some of the inefficiencies associated with aqueous spray mixtures, such as droplets reflecting off the target, in-flight evaporation and droplet dry-down, can be minimised. Rainfastness of the active may also be a problem for some products where the active constituent may be washed off the target by rain some hours after application but before it has been adequately taken up. Other benefits which may be achieved using non-aqueous carriers include enhanced uptake into the target and reduced spray volumes.
30

Herbicide compositions are also applied using planes or helicopters. Much of the cost of aerial spraying is associated with the aircraft set up and flying time, hence to be able to spray highly concentrated compositions over a larger area without reloading multiple times allows for more efficient use of aircraft.

- 5 Glyphosate and other lipophobic herbicides, such as glufosinate, are basically insoluble in lipophilic carriers which would allow exploitation of the lower spray volumes. Thus, there has been a need to develop an essentially non-aqueous carrier system with low volatility for a lipophobic herbicide such as glyphosate.

Summary of the Invention

- 10 It has been found that it is possible to prepare an essentially non-aqueous herbicide composition where a lipophobic herbicide, such as glyphosate, is dissolved in a lipophilic carrier using hydrophobic tertiary amines to form a lipophilic solvent soluble complex. The lipophobic herbicide is not dissolved in an aqueous carrier or in an aqueous carrier dispersed in a lipophilic carrier. The essentially non-aqueous herbicide composition is then
15 suitable for use without dilution in water and may provide a variety of benefits including reduced spray volumes, improved efficacy and rainfastness.

In order to minimise inefficiencies such as in-flight evaporation, the choice of the non-aqueous carrier involves the balance of many factors such as viscosity and volatility. It has further been found that the use of tertiary amines with the lipophobic herbicide enables the
20 use of non-volatile polar solvents. This minimises the possibility that evaporation of the polar solvent will leave the lipophobic herbicide solid on the leaf and essentially unavailable for uptake.

- The herbicide composition according to the invention is suitable for spraying from all known spraying technology including conventional technology used with aqueous
25 solutions.

According to a first aspect of the invention, there is provided an essentially non-aqueous homogeneous liquid herbicide composition comprising:

- (a) a lipophilic solvent soluble complex comprising the reaction product of:
 - (i) not in excess of about 35% by weight of one or more lipophobic herbicides having an acidic moiety; and
 - (ii) not in excess of about 99% by weight of one or more tertiary dimethylamines of the structure $(CH_3)_2N-R$ wherein R contains an alkyl group of at least 8 carbon atoms and may contain other chemical moieties and wherein there is at least one mole equivalent of such amine to each mole of lipophobic herbicide;
- (b) not in excess of about 60% by weight of one or more essentially non-aqueous polar solvents having low volatility;
- (c) not in excess of about 90% by weight of one or more additional solvents selected from the group consisting of low to medium HLB surfactants; and
- (d) not in excess of about 99% by weight of one or more lipophilic carriers.

All proportions are by weight unless otherwise indicated.

The reaction product (a) may be an isolatable product of the reaction of (i) and (ii) or may be formed in situ.

The lipophobic herbicide having an acidic moiety has a chemical structure which includes one or more acid moieties and is therefore capable of reacting with a proton acceptor. Where used herein the term "acid" refers to the Brönsted-Lowry definition of an acid. The term "lipophobic herbicide" therefore includes zwitterionic substances. Examples include glyphosate, glufosinate, bilanfos, fosamine or any other lipophobic herbicide which forms a lipophilic solvent soluble complex with the tertiary amines.

The amount of lipophobic herbicide reacted to form the lipophilic solvent soluble complex is calculated by reference to the free form of the lipophobic herbicide as the active ingredient. The amount of lipophobic herbicide in the composition will typically be determined by the spray rate (litres of spray solution per hectare) and the amount of lipophobic herbicide required to achieve suitable effects. For example, glyphosate is

usually sprayed at 250 to 1000 g/ha with a spray rate of 50 to 100 L/ha or at ultra low volume rates of 2 to 25 l/ha. Preferably, the amount of lipophobic herbicide is not in excess of 25%. More preferably, the amount of lipophobic herbicide is in the range of from 0.1 to 10.0% by weight

- 5 When glyphosate is used, the combination of (i) and (ii) may be considered by some to be mono-, di- or tri- amine salts of glyphosate and such combinations, however prepared, may be used as the source of glyphosate in this composition.

Tertiary amines which are sterically hindered such as tributylamine or didecylmethylamine do not form suitably stable complexes with the lipophobic herbicides. It has also been
10 found that the complexes formed between lipophobic herbicides and amines with considerably less steric hindrance such as primary and secondary alkylamines are difficult to solubilise in lipophilic carriers, prone to crystallisation in essentially non-aqueous environments and require significant amounts of polar solvent to remain liquid in a lipophilic carrier. It is thus surprising that the preferred amines for forming lipophilic
15 solvent soluble complexes with lipophobic herbicides such as glyphosate are tertiary dimethylamines.

The tertiary dimethylamines are of the structure $(CH_3)_2N-R$ wherein R contains an alkyl group of at least 8 carbon atoms and may contain other chemical moieties. For example, the tertiary dimethylamines may be selected from dimethylalkylamines or other substituted
20 alkyldimethylamines such as alkylamidoalkyldimethylamines. Examples of such tertiary dimethylamines are dimethylcocoamine and oleylamidopropyldimethylamine.

Provided that there is at least one mole equivalent of tertiary dimethylamines per mole of lipophobic herbicide, it is possible to use lower amines to react with any remaining acidic moieties on the lipophobic herbicide. Excess amine may be used. Preferably, more than
25 one mole equivalent of tertiary dimethylamine is used per mole of glyphosate because the lipophilic nature of the complex with the lipophobic herbicide increases such that it becomes even easier to dissolve in a chosen lipophilic carrier. The relative amount of additional solvent required to aid in solubilising the complex is also reduced. Therefore,
highly concentrated compositions suited to ultra low volume spraying are possible as there
30 is less additional solvent in proportion to the complex in order to dissolve it in a small amount of lipophilic carrier. Preferably, the amount of amine is in the range of from 1 to

50% by weight. More preferably, the amount of amine is in the range of from 10 to 25% by weight.

The essentially non-aqueous polar solvents having low volatility may be selected from solvents available to those skilled in the art, for example, butane-1,3-diol, hexylene glycol, 5 2-ethylhexanol or dipropylene glycol monomethyl ether. These polar solvents are necessary for the formation of the lipophilic complex of the lipophobic herbicide with the tertiary dimethylamine and subsequent stability of the herbicide composition as a liquid. Typically, the amount of polar solvent is in the range from equal weight to lipophobic herbicide to twice the lipophobic herbicide weight. In a ready-to-use formulation 10 preferably the amount of essentially non-aqueous polar solvents which have low volatility is in the range of from 1 to 10% by weight.

Small portions of volatile polar solvents such as water, ethanol or isopropanol may be used to assist the action of the essentially non-aqueous polar solvents having low volatility. Such volatiles may later be readily removed from the composition if desired. Since these 15 volatile solvents are used in small proportions the overall stability of the composition is not detrimentally effected if the volatile solvent evaporates in use.

The types of reagents which may be used as additional solvents are defined by reference to the term "surfactant", however, it is not necessary that these substances exhibit typical surfactant characteristics when used in the composition particularly given that they are used 20 without dilution in water. All surfactants consist of a molecule that combines both hydrophilic and lipophilic groups. The HLB of a surfactant is an expression of its Hydrophile-Lipophile-Balance, that is, the balance of the size and strength of the hydrophilic and lipophilic groups of the emulsifiers. A surfactant that is predominantly lipophilic is assigned an HLB number in the range 0 – 10 and a surfactant which is 25 predominantly hydrophilic is assigned a higher HLB number above 10.

Examples of suitable surfactants with a low to medium HLB which may be used as additional solvents are mono and di-glycerides of fat forming fatty acids (glycerol monooleate or glycerol dioleate), partial fatty acid esters of sorbitol anhydrides (sorbitan monooleate or sorbitan monolaurate), partial fatty acid esters of other polyols such as 30 pentaerythritol, polyglycerol and sugar pentitols, hexitols and their anhydrides and lecithin. Further examples include low mole nonionic ethoxylates with alkyl or arylalkyl of 12 to 21

carbon atoms and 2 to 9 moles ethylene oxide adducted, such as Teric 12A3 (C12 or C12 - 15 alcohol with 3 moles ethylene oxide) and Teric DD5 (dodecylphenol with 5 moles ethyleneoxide). Still further examples include fatty alkanolamides such as oleic diethanolamide, organopolysiloxanes or alkylpolyglycosides

- 5 Preferably, there is not in excess of 50% by weight of additional solvents. More preferably, the amount of additional solvents is in the range of from 0.4 to 40.0% by weight. The very low levels of these additional solvents will be present if commercial spray oil is used as the lipophilic carrier since adjuvant compositions such as crop oil concentrates or other self-emulsifying oil-based compositions already contain these surfactants. The amount of
10 additional solvent used from half of the combined weight of lipophobic herbicide, amine and polar solvent to about 1.5 times this weight.

The lipophilic carrier may be any suitable lipophilic carriers known to those skilled in the art. For example, the lipophilic carrier may be petroleum fractions, vegetable oils, synthetic triglycerides, alkyl esters of fatty acids, fatty alcohols, guerbet alcohols or any
15 mixture thereof. Preferably, the lipophilic carriers are aliphatic paraffinic light distillates or vegetable oils and their derivatives. Typically, a petroleum fraction is used as it has been cost effective. These fractions, for example, can be 70, 100 or 150 second solvent neutral. Preferably, there is not in excess of 99% by weight of lipophilic carrier. If the composition is applied to herbicide resistant crops, then preferably, the lipophilic carrier is low in
20 aromatics. Vegetable oils and their derivatives may be preferred for ecological reasons. The choice of the lipophilic carrier may be influenced by its viscosity and the spray application technology.

In another embodiment of the invention, the herbicide composition is a concentrated composition comprising reagents (a) and (b), which could itself be sprayed or it could be
25 diluted later with an essentially non-aqueous carrier such as reagent (c) and optionally (d). For example, the concentrated composition could be sold in containers of convenient size and farmers could then dilute the composition with a crop oil concentrate as desired for the spraying technique to be used. The invention includes a concentrate composition comprising additional solvents wherein the additional solvents may act as the carrier. Such
30 compositions may be sprayed without addition of further solvent or may be diluted with an essentially non-aqueous lipophilic carrier. Where little or no lipophilic carrier is added

then lesser amounts of additional solvents are appropriate and facilitate the more concentrated lipophobic herbicide preparations used in ultra low volume spraying.

The following table sets out the proportions of components which are typical for essentially non-aqueous glyphosate compositions intended for conventional volume, low volume and 5 ultra low volume spray application.

Similar principles apply to the formation of lipophilic compositions based on complexes of glufosinate.

Component	conventional volume spray application			low volume spray application			ultra low volume spray application		
	50 – 100 l/ha	25 – 50 l/ha	2 – 25 l/ha	min	typical	max	min	typical	max
glyphosate	0.1	1	5	0.1	2	10	0.2	5	25
3° amine	0.1	4	25	0.4	8	40	0.8	15	50
polar solvent	0.1	1	10	0.1	2	20	0.2	5	50
additional solvent	0.1	9	30	1	15	90	2	25	90
lipophilic carrier	50	85	99	0	73	98	0	50	95

10 In another preferred form of the invention, the herbicide composition further comprises one or more pesticides which are compatible with the lipophilic nature of the herbicide composition. The term "pesticides" includes herbicides, fungicides and insecticides. For example, 2,4-D may be added to the composition. In some situations, glyphosate, for example, alone is not sufficient to address the farmer's needs and a lipophilic 15 herbicide is combined with the glyphosate composition.

In another preferred form of the invention, the herbicide composition further comprises one or more other available adjuvant components. The adjuvant component may be selected from plant nutrients, spray drift retardants, stickers, spreaders or viscosity modifiers.

- 5 Non-aqueous solutions of lipophobic herbicides can thus be formed for spray application in situations where water evaporation or spray volume may be an issue.

According to a second aspect of the invention, there is provided a method for improving rainfastness of a lipophobic herbicide comprising the step of formulating the lipophobic herbicide in an essentially non-aqueous composition comprising:

- 10 (a) a lipophilic solvent soluble complex comprising the reaction product of:
- (i) not in excess of about 35% by weight of one or more lipophobic herbicides having an acidic moiety; and
 - (ii) not in excess of about 99% by weight of one or more tertiary dimethylamines of the structure $(CH_3)_2N-R$ wherein R contains an alkyl group of at least 8 carbon atoms and may contain other chemical moieties and wherein there is at least one mole equivalent of such amine to each mole of lipophobic herbicide;
- 15 (b) not in excess of about 60% by weight of one or more essentially non-aqueous polar solvents having low volatility;
- 20 (c) not in excess of about 90% by weight of one or more additional solvents selected from the group consisting of low to medium HLB surfactants; and
- (d) not in excess of about 99% by weight of one or more lipophilic carriers.

- According to a third aspect of the invention, there is provided a method for treating weeds comprising the step of applying an essentially non-aqueous herbicide composition
- 25 comprising:

- (a) a lipophilic solvent soluble complex comprising the reaction product of:
 - (i) not in excess of about 35% by weight of one or more lipophobic herbicides having an acidic moiety; and

- 5 (ii) not in excess of about 99% by weight of one or more tertiary dimethylamines of the structure $(CH_3)_2N-R$ wherein R contains an alkyl group of at least 8 carbon atoms and may contain other chemical moieties and wherein there is at least one mole equivalent of such amine to each mole of lipophobic herbicide;
- 10 (b) not in excess of about 60% by weight of one or more essentially non-aqueous polar solvents having low volatility;
- (c) not in excess of about 90% by weight of one or more additional solvents selected from the group consisting of low to medium HLB surfactants; and
- (d) not in excess of about 99% by weight of one or more lipophilic carriers.

According to a fourth aspect of the invention, there is provided a method for preparing an essentially non-aqueous sprayable herbicide composition comprising the steps of

- 15 (a) combining the following reagents:
- (i) not in excess of about 35% by weight of one or more lipophobic herbicides having an acidic moiety; and
- 20 (ii) not in excess of about 99% by weight of one or more tertiary dimethylamines of the structure $(CH_3)_2N-R$ wherein R contains an alkyl group of at least 8 carbon atoms and may contain other chemical moieties and wherein there is at least one mole equivalent of such amine to each mole of lipophobic herbicide; and
- (iii) not in excess of about 60% by weight of one or more essentially non-aqueous polar solvents having low volatility;
- 25 (b) combining the mixture formed in (a) with not in excess of about 90% by weight one or more additional solvents selected from the group consisting of low to medium HLB surfactants and not in excess of about 99% by weight one or more lipophilic carriers.

Preferably, the reagents in step (a) are combined with heating/stirring. Reflux conditions may be used where appropriate. Preferably, the combining in step (b) comprises stirring the mixture whilst warm.

In a further embodiment, the lipophilic solvent soluble complex is prepared and isolated from the essentially non-aqueous polar solvent prior to its use. This is useful where the essentially non-aqueous polar solvent being used is inconvenient as a component of the herbicide composition, for example, due to product registration requirements, and it is
5 preferable that it be removed.

According to a fifth aspect of the invention, there is provided an essentially non-aqueous homogeneous liquid herbicide composition comprising:

- (a) a lipophilic solvent soluble complex comprising the reaction product of:
 - (i) not in excess of about 35% by weight of one or more lipophobic herbicides having an acidic moiety; and
 - (ii) not in excess of about 99% by weight of one or more tertiary dimethylamines of the structure $(CH_3)_2N-R$ wherein R contains an alkyl group of at least 8 carbon atoms and may contain other chemical moieties and wherein there is at least one mole equivalent of such amine to each mole of lipophobic herbicide; and
- (b) not in excess of about 60% by weight of one or more essentially non-aqueous polar solvents which assist the formation of the lipophilic solvent soluble complex, wherein the complex is formed in the presence of the essentially non-aqueous polar solvent but the essentially non-aqueous polar solvent may be removed after formation of the complex if desired.
20

According to a sixth aspect of the invention, there is provided an essentially non-aqueous homogeneous liquid herbicide composition comprising:

- (a) a lipophilic solvent soluble complex comprising the reaction product of:
 - (i) not in excess of about 35% by weight of one or more lipophobic herbicides having an acidic moiety; and
 - (ii) not in excess of about 99% by weight of one or more tertiary dimethylamines of the structure $(CH_3)_2N-R$ wherein R contains an alkyl group of at least 8 carbon atoms and may contain other chemical moieties and wherein there is at least one mole equivalent of such amine to each mole of lipophobic herbicide;
30

12

- (b) not in excess of about 90% by weight of one or more additional solvents selected from the group consisting of low to medium HLB surfactants; and
- (c) not in excess of about 99% by weight of one or more lipophilic carriers.

It has also been found that it is possible to use a lower amount of tertiary dimethylamines
5 and still obtain an essentially non-aqueous homogeneous liquid herbicide composition.

According to a seventh aspect of the invention there is provided an essentially non-aqueous homogeneous liquid herbicide composition comprising:

- (a) a lipophilic solvent soluble complex comprising the reaction product of:
 - (i) not in excess of about 50% by weight of one or more lipophobic herbicides having an acidic moiety; and
 - (ii) not in excess of about 99% by weight of one or more tertiary dimethylamines of the structure $(CH_3)_2N-R$ wherein R contains an alkyl group of at least 8 carbon atoms and may contain other chemical moieties, wherein there is less than one mole equivalent of such amines to each mole of lipophobic herbicide;
 - (iii) not in excess of about 20% by weight of one or more hydrophilic amines;wherein the total mole equivalents of the amines in (ii) and (iii) is at least equivalent to the moles of lipophobic herbicide;
- (b) not in excess of about 60% by weight of one or more essentially non-aqueous polar solvents having low volatility;
- (c) not in excess of about 90% by weight of one or more additional solvents selected from the group consisting of low to medium HLB surfactants; and
- (d) not in excess of about 99% by weight of one or more lipophilic carriers.

25 Examples of hydrophilic amines include those conventionally used with aqueous glyphosate preparations, eg. Isopropylamine, diethanolamine and monoethanolamine.

Examples

The invention will now be further illustrated and explained in the following non-limiting examples.

The following components were used.

Ammonium nitrate (adjuvant component)	Ex Orica, Australia
Break-thru OE 444 (additional solvent)	Organosilicon ex Goldschmidt, USA
BS 1000 (used in control treatments)	Commercial wetting agent ex Cropcare, Australia
1,3-butanediol (polar solvent)	Ex Hoechst Celanese, USA
2,4-D (herbicide)	2,4-D acid ex Unisun, China
Diethanolamine (hydrophilic amine)	Ex Union Carbide
Dimethylcocoamine (tertiary dimethylamine)	Ex Proctor & Gamble, USA
Esterol 123 (lipophilic solvent)	Ethyl oleate (80% ethyl/20% methyl) ex Victorian Chemical Company, Australia
Esterol 272 (additional solvent)	Glyceryl mono-oleate ex Victorian Chemical Company, Australia
Ethanol (volatile solvent)	Anhydrous, 100SGF3 grade methanol denatured ex CSR, Australia
Glufosinate (lipophobic herbicide)	3-amino-3-(carboxypropyl)methylphosphonic acid ex Aventis,
Glyphosate (lipophobic herbicide)	N-(phosphonomethyl)glycine (98% minimum) ex Davison Industries, Australia or Unisun Chemicals, China
Glysolv DPM (polar solvent)	Dipropylene glycol monomethyl ether ex Huntsman, Australia
Hexylene glycol (polar solvent)	Ex Tiger Chemicals, Australia

Iso-octanol (polar solvent)	Ex Bentley-Chemplax, Australia
Monoethanolamine (hydrophilic amine)	Ex Union Carbide
Oleylamidopropyldimethylamine (tertiary dimethylamine)	Prepared by reaction of oleic acid with N,N-dimethylaminopropylamine at Victorian Chemical Company, Australia
Phosphoric acid 81% aqueous	Ex Deltrex Chemicals, Australia
Prorex 36 (lipophilic carrier)	100 solvent neutral mineral oil Ex Mobil, Australia
Shell P878 (lipophilic carrier)	300 test kerosene ex Shell, Australia
Span 80 (additional solvent)	Sorbitan mono-oleate ex Huntsman Corporation, Australia
Teric 12A3 (additional solvent)	C12-15 synthetic alcohols and 3 moles ethylene oxide ex Huntsman Corporation, Australia
Teric DD5 (additional solvent)	dodecylphenol and 5 moles ethylene oxide ex Huntsman Corporation, Australia
Terwet 3001 (additional solvent)	Alkyl polyglucoside ex Huntsman, Australia
Vicamid 825 (additional solvent)	Oleyldiethanolamide ex Victorian Chemical Company, Australia
VOC RHT 70 (lipophilic carrier)	70 solvent neutral mineral oil ex Safety-Kleen, USA

Example 1

62.5 parts dimethylcocoamine, 15 parts glyphosate, 15 parts 1,3-butanediol and 7.5 parts ethanol were refluxed together for 15 minutes to form a single phase liquid with about 15% of glyphosate present.

This formulae is useful when high glyphosate content is required. For example, this formula is appropriate for use in ultra low volume crop spraying.

Example 2

The following compositions were prepared and resulted in clear liquids containing about
 5 7.5% glyphosate. The dimethylcocoamine, ethanol and glyphosate were refluxed together
 to form a single phase liquid. The additional solvent was then added and mixing continued
 at 40 to 70°C. These compositions may be used for ultra low volume spray application
 directly. They are also soluble in VOC RHT 70 and therefore can be converted to
 compositions suitable for low volume spray application. However, loss of ethanol from
 10 these formulations resulted in unstable compositions.

Composition	1	2	3
Dimethylcocoamine	33	33	33
Ethanol	9	9	9
Glyphosate	7.5	7.5	7.5
Span 80	-	-	50.5
Teric DD5	-	50.5	-
Teric 12A3	50.5	-	-

Example 3

32 parts dimethylcocoamine, 8 parts 1,3-butanediol and 8 parts glyphosate were mixed
 15 together at 60°C for one hour. 24 parts Span 80, 2 parts Glyolv DPM and 26 parts Esterol
 272 were then added and mixing continued at 40 to 70°C until a clear liquid was formed
 with about 8% glyphosate acid.

This composition is soluble in VOC RHT 70 if a more dilute composition is desired.

Use of 1,3-butanediol rather than ethanol minimised the vapour loss during formation of the composition.

Example 4

- 2 parts glyphosate was combined with 8 parts dimethylcocoamine and 4 parts ethanol and
5 refluxed with stirring until clear to form Mixture A. When cooled, Mixture A was a liquid
paste with about 14-15% glyphosate.
- 20 parts of Esterol 272 was added to Mixture A and warmed at 30 to 50°C with stirring
until clear to form Mixture B. When cooled, Mixture B was a clear viscous liquid with
about 5-6% glyphosate.
- 10 34 parts of Mixture B was combined with 66 parts of VOC RHT 70 to provide a clear
liquid with 2% glyphosate.

If 340 parts of Mixture B is diluted to 1 litre with VOC RHT 70, a preparation containing
2% w/v suitable for spraying is obtained.

- 15 If 340 parts of Mixture B is diluted to 4 litres with VOC RHT 70, a preparation containing
0.5% w/v suitable for spraying is obtained.

Example 5

- 79 parts of dimethylcocoamine was combined with 21 parts of glyphosate and 40 parts
ethanol and refluxed until a clear solution was formed. 210 parts of Esterol 272, 15 parts
of Break-thru OE 444 and 635 parts of VOC RHT 70 were added with mixing at 30 to
20 50°C. The final product was a clear liquid with about 2% glyphosate present.

Example 6

- 90 parts of dimethylcocoamine was combined with 20 parts glyphosate and 30 parts
ethanol and refluxed until a clear solution was formed. 195 parts of Esterol 272, 15 parts
Teric DD5 (or Teric 12A3) and 650 parts VOC RHT 70 were then added with mixing at 30
25 to 50°C. The final product was 1000 parts of a clear liquid with about 2% glyphosate
present.

This formulation enables farmers and/or aerial operators to use self-emulsifying mineral oil compositions that contain surfactants, such as crop oil concentrates, as the lipophilic carrier when preparing the composition.

Example 7

5 Glyphosate (50 parts), 1,3-butanediol (50 parts), ethanol (50 parts) and dimethylcocoamine (132 parts, approximately 2.14 molar equivalent to glyphosate) were refluxed at 80-90°C with stirring for 90 minutes until clear to form Mixture C. Mixture C was a clear liquid with 17-18% glyphosate.

Mixture C (20 parts) was combined with Esterol 272 (30 parts) to provide a clear liquid
10 with 7% glyphosate.

Mixture C (24g) was combined with Esterol 272 (36g) and a sufficient amount of Shell P878 to provide 200 ml of a clear liquid with 2% w/v glyphosate.

Example 8

Glyphosate (50 parts), 1,3-butanediol (50 parts), ethanol (50 parts), dimethylcocoamine (71 parts, approximately 1.07 molar equivalent to glyphosate) and water (20 parts) were refluxed at 80-90°C with stirring for one hour. Esterol 272 (118 parts), Vicamid 825 (66 parts) and Span 80 (57 parts) were then added and the mixture warmed with stirring to form Mixture D, a clear liquid with 10-11% glyphosate.

Mixture D (40g) was combined with a sufficient amount of Shell P878 to form 200 ml of a
20 clear liquid with 2% w/v glyphosate.

Example 9

In this example, compositions containing different lipophobic herbicides were tested. The amount of herbicide per hectare was lowered to below the typical application rate to enable an assessment of the difference effectiveness of the compositions.

25 The inclusion of non-volatile polar solvents was considered essential for these and subsequent formulations following instability problems noted with earlier compositions upon loss of ethanol.

The following compositions were tested.

Composition	Lipophobic herbicides (g/L)	Dimethylcocoamine (g/L)	Polar solvent (g/L)	Additional solvent (g/L)	Lipophilic carrier (to 1 litre)			
4.	Glyphosate (25 g/ha)	2.59	3.69	1,3-butanediol	2.59	Esterol 272	31.1	VOC RHT 70
				Ethanol	2.59	Span 80	2.95	
				Water	1.04	Vicamid 825	3.42	
5.	Glyphosate (75g/ha)	7.68	10.91	1,3-butanediol	7.68	Esterol 272	64.07	VOC RHT 70
				Ethanol	7.68	Span 80	8.75	
				Water	3.06	Vicamid 825	10.14	
6.	Glyphosate (150 g/ha)	15.36	21.82	1,3-butanediol	15.36	Esterol 272	68.14	VOC RHT 70
				Ethanol	15.36	Span 80	17.5	
				Water	6.12	Vicamid 825	20.28	
7.	Glyphosate (25 g/ha)	2.57	7.29	1,3-butanediol	2.57	Esterol 272	30	VOC RHT 70
				Ethanol	2.57			

Composition	Lipophobic herbicides (g/L)	Dimethylcocoamine (g/L)	Polar solvent (g/L)	Additional solvent (g/L)	Lipophilic carrier (to 1 litre)			
8.	Glyphosate (75g/ha)	7.71	21.87	1,3 butanediol	7.71	Esterol 272	50	VOC RHT 70
				Ethanol	7.71			
9.	Glyphosate (150 g/ha)	15.42	43.74	1,3 butanediol	15.42	Esterol 272	60	VOC RHT 70
				Ethanol	15.42			
10.	Glyphosate (25 g/ha)	2.57	10.26	1,3 butanediol	2.97	Vicamid 825	60	VOC RHT 70
				Water	50	Teric 12A3	65	
11.	Glyphosate (75g/ha)	7.71	30.87	1,3 butanediol	8.92	Vicamid 825	80	VOC RHT 70
				Water	50	Teric 12A3	65	
12.	Glyphosate (25 g/ha)	2.57	10.26	1,3 butanediol	2.97	Esterol 272	24.2	Esterol 123
13.	Glyphosate (75g/ha)	7.71	30.87	1,3 butanediol	8.92	Esterol 272	52.5	Esterol 123
14.	Glyphosate (150 g/ha)	15.42	61.73	1,3 butanediol	17.85	Esterol 272	65	Esterol 123

Composition	Lipophobic herbicides (g/L)		(g/L)	Polar solvent (g/L)	Additional solvent (g/L)		Lipophilic carrier (to 1 litre)
22.	Glyphosate (75 g/ha)	7.5	45	1,3 butanediol	20	Esterol 272	90
	2,4-D (150 g/ha)	15					VOC RHT 70

The following control treatments were used. Glyphosate refers to Glyphosate CT (containing 450 g/l glyphosate as the isopropylamine salt), 2,4-D refers to Amicide 500 (containing 2,4-D 500 g/l as the dimethylamine salt) and Glufosinate refers to BASTA (containing glufosinate-ammonium 200 g/l). Control 7 assesses the damage caused by the
5 lipophilic composition with citric acid substituted for the herbicide.

Control 1	25g/ha glyphosate in aqueous solution with 0.1 % BS 1000
Control 2	75 g/ha glyphosate in aqueous solution with 0.1 % BS 1000
Control 3	150 g/ha glyphosate in aqueous solution with 0.1 % BS 1000
Control 4	VOC RHT 70
Control 5	Esterol 123
Control 6	Glyphosate(75g/ha), 2,4-D (150g/ha) in aqueous solution with 0.1 % BS 1000
Control 7	20 g/L citric acid, 20 g/L 1,3-butanediol, 70 g/L dimethylcocoamine, 100 g/L Esterol 272 and VOC RHT 70 to 1 litre.
Control 8	Glyphosate(75g/ha), 2,4-D (75g/ha) in aqueous solution with 0.1 % BS 1000
Control 9	Glyphosate(150g/ha), 2,4-D (150g/ha) in aqueous solution with 0.1 % BS 1000
Control 10	Glufosinate (50 g/ha)
Control 11	Glufosinate (200 g/ha)

Control 12	2,4-D (150 g/ha)
------------	------------------

Method

The treatments were applied to Ryegrass and/or Spiny Emex in both standard conditions and with simulated 10 mm rain two hours after spraying. Each test had 7 replicates. The 5 plants were assessed 14 days after spraying.

The control treatments containing herbicides were diluted in water and applied at a rate of 64 l/Ha. The test essentially non-aqueous compositions were applied directly at a rate of 10 l/Ha.

Results

- 10 A hyphen (-) means that the composition was tested in those circumstances.

Treatment	Fresh weight (g/plant)			
	Ryegrass with no rain	Ryegrass with rain	Spiny Emex with no rain	Spiny Emex with rain
No treatment	2.07	2.07	10.4	10.44
Control 1	1.162	1.564	-	-
Control 2	0.308	1.192	8.32	10.37
Control 3	0.236	0.5000	6.04	9.02
Control 4	1.142	-	11.6	-
Control 5	1.443	-	-	-
Control 6	0.417	1.198	5.53	9.91
Control 7	1.50	-	12.3	-
Control 8	-	-	6.93	10.19
Control 9	-	-	5.71	8.55
Control 10	-	-	8.59	11.05
Control 11	-	-	1.26	10.07
Control 12	-	-	9.27	7.52
Composition 4.	0.895	-	-	-
Composition 5.	0.183	-	-	-

Treatment	Fresh weight (g/plant)			
	Ryegrass with no rain	Ryegrass with rain	Spiny Emex with no rain	Spiny Emex with rain
Composition 6.	0.117	-	-	-
Composition 7.	0.339	-	-	-
Composition 8.	0.261	-	-	-
Composition 9.	0.106	-	-	-
Composition 10.	0.311	-	-	-
Composition 11.	0.292	-	-	-
Composition 12.	0.338	0.682	-	-
Composition 13.	0.124	0.254	-	-
Composition 14.	0.133	0.224	-	-
Composition 15.	0.390	0.614	-	-
Composition 16.	0.117	0.197	5.13	4.56
Composition 17.	0.104	0.321	2.11	2.95
Composition 18.	-	-	4.78	7.37
Composition 19.	-	-	3.71	4.44
Composition 20.	-	-	4.16	4.58
Composition 21.	-	-	3.42	3.26
Composition 22.	0.1543	0.978	4.08	6.59

LSD (P=0.05) 0.300

Conclusions

(a) Glyphosate

At the three concentration levels of 25, 75 and 150 g/Ha, the test compositions performed better than the control treatments on Ryegrass with no rain. In rain conditions, the test compositions 12 to 17 performed significantly better than the control treatments and indeed are comparable with or outperform the control treatments 1-3 without rain.

Compositions 10 and 11 which contained water did not provide improved results over those without water.

On Spiny Emex, at the concentration levels of 75 and 150 g/Ha, test compositions 16 and 17 performed markedly better than the control treatments 2–3 in both no rain and rain conditions. The control treatments were not effective to control Spiny Emex in rain conditions, however test compositions 16 and 17 in rain conditions outperformed the
5 control treatments without rain.

Therefore, the compositions of the invention provided rainfastness for the herbicide.

(b) Glyphosate and 2,4-D

Composition 22 on Ryegrass performed better than Control 6 both with rain and without rain.

10 On Spiny Emex, Compositions 20 to 22 performed better than Controls 6, 8 and 9. Again, the control treatments were not effective to control Spiny Emex in rain conditions, but the compositions of the invention in the rain were comparable or outperformed with the control treatments without rain indicating that the composition of the invention provided rainfastness for the herbicide.

15 (c) Glufosinate

Without rain on Spiny Emex, Composition 18 performed better than Control 10 therefore the composition of the invention provides an adjuvant effect at a concentration of 50g/Ha of glufosinate.

In rain, Compositions 18 and 19 performed better than Controls 10 and 11 which were not
20 effective at controlling Spiny Emex. Therefore, the compositions of the invention provided rainfastness for the herbicide.

Example 10

In this example, essentially non-aqueous compositions containing glyphosate were tested for efficacy.

25 The following compositions were tested.

			Polar solvent (g/L)		Additional solvent (g/L)		Lipophilic carrier (to 1 litre)
Composition		Dimethylcocoamine (g/L)					
23.	21	79.1	1,3 butanediol	24	Breakthru OE 444	16	VOC RHT 70
			Glysolv DPM	9	Esterol 272	47	
					Span 80	46.5	
24.	5.25	19.8	1,3 butanediol	6	Breakthru OE 444	16	VOC RHT 70
			Glysolv DPM	2	Esterol 272	21.5	
					Span 80	11.5	
25.	2.1	7.91	1,3 butanediol	2.4	Breakthru OE 444	16	VOC RHT 70
					Esterol 272	12.5	
			Glysolv DPM	1	Span 80	5	
26.	21	90	1,3 butanediol	24	Esterol 272	10	VOC RHT 70
					Teric 12A3	60	
					Teric DD5	30	
27.	5.25	22.5	1,3 butanediol	6	Esterol 272	10	VOC RHT 70
					Span 80	5	
					Teric 12A3	15	
					Teric DD5	7.5	
28.	2.1	9	1,3 butanediol	2.4	Esterol 272	5	VOC RHT 70
					Span 80	7.5	
					Teric 12A3	10	
					Teric DD5	5	

Composition	Dimethylcocoamine (g/L)	Polar solvent (g/L)	Additional solvent (g/L)	Lipophilic carrier (to 1 litre)			
29.	21.1	84.4	1,3 butanediol	24.5	Esterol 272	43.3	Shell P878
			Glyolv DPM	9.3	Span 80	43.3	
30.	5.3	21.1	1,3 butanediol	6.1	Esterol 272	19	Shell P878
			Glyolv DPM	2	Span 80	14	
31.	2.11	8.44	1,3 butanediol	2.45	Esterol 272	12.5	Shell P878
			Glyolv DPM	1	Span 80	10	
32.	21.1	84.4	1,3 butanediol	24.5	Teric 12A3	45	Shell P878
			(Ammonium nitrate 20)	50	Teric DD5	10	
					Terwet 3001	22.5	
					Vicamid 825	50	
33.	5.3	21.1	1,3 butanediol	6.1	Teric 12A3	45	Shell P878
			(Ammonium nitrate 20)	50	Teric DD5	10	
					Terwet 3001	22.5	
					Vicamid 825	50	
34.	2.11	8.44	1,3 butanediol	2.45	Teric 12A3	45	Shell P878
			(Ammonium nitrate 20)	50	Teric DD5	10	
					Terwet 3001	22.5	
					Vicamid 825	50	

The following control treatments were used.

Control 1	50 g/ha glyphosate in aqueous solution with 0.1 % BS 1000
Control 2	125 g/ha glyphosate in aqueous solution with 0.1 % BS 1000
Control 3	500 g/ha glyphosate in aqueous solution with 0.1 % BS 1000

Method

The treatments were applied to ryegrass in conditions equivalent to no rain and 10 mm rain
5 two hours after spraying. Each test had 7 replicates. The plants were assessed 14 days
after spraying.

The control treatments containing herbicides were applied at a rate of 64 l/Ha according to
current practice.

The test essentially non-aqueous compositions were too viscous for spraying and were
10 diluted 1:1 with Shell P878 and sprayed at 50 l/ha.

Results

Treatment	Fresh weight (g/plant)	
	Ryegrass with no rain	Ryegrass with rain
No treatment	1.862	1.862
Control 1	0.969	1.268
Control 2	0.281	0.663
Control 3	0.234	0.309
Blank oil	1.093	-
Composition 23.	0.217	0.181
Composition 24.	0.286	0.211
Composition 25.	0.381	0.389
Composition 26.	0.194	0.203
Composition 27.	0.284	0.292
Composition 28.	0.362	0.411

Treatment	Fresh weight (g/plant)	
	Ryegrass with no rain	Ryegrass with rain
Composition 29.	0.260	0.218
Composition 30.	0.404	0.322
Composition 31.	0.323	0.748
Composition 32.	0.481	0.385
Composition 33.	0.281	0.208
Composition 34.	0.375	0.313

LSD (P=0.05) 0.191

Conclusions

The test results show that glyphosate is active in a non-aqueous environment with comparable or better results.

- 5 Rainfall after application is known to reduce the efficacy of certain products including glyphosate-based herbicides. This is evidenced by comparing the results for the commercial products with and without simulated rainfall as shown in the above Table where the Fresh Weight for each of the Controls 1, 2 and 3 is higher for each example where rain is applied. By contrast, the non-aqueous Compositions 23 to 30 do not show
10 such loss of activity when simulated rainfall was applied and can be said to be rainfast.

Example 11

In this example, essentially non-aqueous compositions containing glyphosate were tested for efficacy.

The following compositions were tested. In the table the following abbreviations are used:

DMC	Dimethylcocoamine (tertiary)
OAPA	Oleylamidopropyldimethylamine (tertiary)
DEA	Diethanolamine (hydrophilic)
MEA	Monoethanolamine (hydrophilic)

Composition	Glyphosate (g)	Amine (g)		Polar solvent (g)		Additional solvent (g)		Lipophilic carrier (to 2 litre)
35.	10.2	DMC	27	1,3-butanediol hexylene glycol	10 12	Esterol 272	60	VOC RHT 70
36.	10.2	DMC	14	1,3-butanediol 2-ethylhexanol	4 4	Esterol 272	35	VOC RHT 70
		DEA	0.6	Ethanol water	2 3	Vicamid 825	35	
37.	10.2	OAPA	31	1,3-butanediol Water Glyolv DPM	5 5 7.5	Esterol 272	76	VOC RHT 70
38.	10.2	OAPA	45	1,3-butanediol water	5 5	Vicamid 825 Esterol 272	15 100	VOC RHT 70
39.	10.2	OAPA	2.8	1,3-butanediol	5.6	Vicamid 825	30	Prorex 36 3 and VOC RHT 70
		MEA	4	water	7.5	Esterol 272	32.8	
40.	10.2	DMC	2	1,3-butanediol	5.6	Vicamid 825	25	Prorex 36 3 and VOC RHT 70
		MEA	4	water	7.5	Esterol 272	29	

Composition 35 to 40 each have 0.5% w/v glyphosate. These treatments were sprayed at 50l/ha to give 50g/ha of glyphosate under standard conditions and with 5mm simulated rain 2 hours after application. Control 2 was sprayed in equivalent amounts.

- 5 The above compositions are being tested against the following control treatment.

Control 1	Roundup Max (glyphosate 510g/l as the MEA salt) diluted in water and sprayed at 64l/ha to give 50 and 150 g/ha of glyphosate.
Control 2	50g water, 30g citric acid, 30g 1,3-butanediol, 30g hexylene glycol, 90g Vicamid 825, 70g Oleylamidopropyltrimethylamine, 210g Esterol 272 VOC RHT 70 to 2L.

Results

Each test had seven replicates and the plants were assessed 14 days after spraying.

Treatment	Fresh weight (g)	
	Standard conditions	5mm rain
No treatment	3.42	
Control 1 (50 g/ha)	1.07	2.88
Control 1 (150 g/ha)	0.74	1.40
Control 2	2.49	3.37
Composition 35.	1.47	1.85
Composition 36.	1.61	1.42
Composition 37.	1.16	1.78
Composition 38.	0.76	1.06
Composition 39.	0.89	2.60
Composition 40.	1.48	3.75

LSD (P=0.05) 0.78

Conclusion

Examples 35 to 38 all contain at least one mole equivalent of tertiary dimethylamine to each mole of glyphosate. Examples 39 and 40 contain less than one (approx 0.16 mole equivalent for each) mole equivalent of tertiary dimethylamine to each mole of glyphosate with the remainder of the glyphosate being complexed with the hydrophilic amine monoethanolamine in accordance with the sixth aspect of the invention.

Each of the examples 35 to 40 show similar efficacy to the commercial product Round-Up Max under the Standard Conditions.

10 Examples 35 to 38 are less affected by simulated rainfall than examples 39 and 40 or the Control 1. The increase in fresh weight is up to 50% for examples 35 to 38 (reduction seen for 36) whilst for each of Examples 39, 40 and Control 1, the increase in fresh weight is greater than 100%. Examples 35 to 38 or compositions containing at least one mole equivalent of tertiary dimethylamine to each mole of glyphosate are more rainfast than
15 other lipophilic compositions or the aqueous control.

Example 12

Most of the compositions shown in the previous examples have been designed to be tested at sublethal doses of the herbicide for comparative testing, or are suitable as herbicidal compositions when sprayed at rates considerably greater than 10 l/ha.

20 The following Compositions 41 to 46 have been prepared as examples of essentially non-aqueous herbicide compositions each containing 50 g/l of the herbicide glyphosate. These examples are considered to be suitable herbicidal compositions for spraying at 10 l/ha to provide 500 g/ha of the active.

In the table the following abbreviations are used:

DMC	Dimethylcocoamine (tertiary)
OAPA	Oleylamidopropyldimethylamine (tertiary)

DEA	Diethanolamine (hydrophilic)
MEA	Monoethanolamine (hydrophilic)

Composition	Glyphosate (g)	Amine (g)	Polar solvent (g)	Additional solvent (g)		Lipophilic carrier (to 100ml)		
41.	5.1	DMC	13.5	1,3-butanediol	5	VOC RHT 70		
				hexylene glycol	5			
42.	5.1	DMC	13.5	1,3-butanediol	5	Esterol 272	12.5	VOC RHT 70
				hexylene glycol	5	Breakthru OE444	0.6	
43.	5.1	DMC	7	1,3-butanediol	2	Esterol 272	12	VOC RHT 70
		DEA	0.3	2-ethylhexanol	2	Vicamid 825	13	
44.	5.1	DMC	1.0	1,3-butanediol	2.8	Vicamid 825	8	VOC RHT 70
		DEA	2.0	water	3.7	Esterol 272	9	
45.	5.1	OAPA	22.7	1,3-butanediol	3.6	Esterol 272	21.6	VOC RHT 70
				Glysolv DPM	5.4			
46.	5.1	OAPA	22.7	1,3-butanediol	3.6	Esterol 272	21.6	Esterol 123
				Glysolv DPM	5.4			

Example 13

In this example, a composition containing glyphosate and 2,4-D was prepared.

Glyphosate	51 parts
2,4-D octyl ester	38 parts
Water	2 parts
1,3-butanediol	20 parts
Dimethylcocamine	121 parts

The final composition contained 19.9% w/v glyphosate. This was a concentrated
5 composition suitable for sale to farmers who may then further dilute the composition with additional solvents and lipophilic carriers or with a crop oil concentrate.

The word 'comprising' and forms of the word 'comprising' as used in this description does not limit the invention claimed to exclude any variants or additions.

Modifications and improvements to the invention will be readily apparent to those skilled
10 in the art. Such modifications and improvements are intended to be within the scope of this invention.

WHAT IS CLAIMED IS:

1. An essentially non-aqueous homogeneous liquid herbicide composition comprising:
 - (a) a lipophilic solvent soluble complex comprising the reaction product of:
 - (i) not in excess of about 35% by weight of one or more lipophobic herbicides having an acidic moiety; and
 - (ii) not in excess of about 99% by weight of one or more tertiary dimethylamines of the structure $(CH_3)_2N-R$ wherein R contains an alkyl group of at least 8 carbon atoms and may contain other chemical moieties and wherein there is at least one mole equivalent of such amine to each mole of lipophobic herbicide;
 - (b) not in excess of about 60% by weight of one or more essentially non-aqueous polar solvents having low volatility;
 - (c) not in excess of about 90% by weight of one or more additional solvents selected from the group consisting of low to medium HLB surfactants; and
 - (d) not in excess of about 99% by weight of one or more lipophilic carriers.
2. A composition according to claim 1 wherein the lipophobic herbicide is selected from the group comprising glyphosate, glufosinate, bilanfos, fosamine or mixtures thereof.
3. A composition according to claim 2 wherein the lipophobic herbicide is glyphosate.
- 20 4. A composition according to claim 2 wherein the lipophobic herbicide is glufosinate.
5. A composition according to claim 1 wherein the amount of lipophobic herbicide is not in excess of 25% by weight.
6. A composition according to claim 1 wherein the amount of lipophobic herbicide is in the range of from 0.1 to 10% by weight.
- 25 7. A composition according to claim 1 wherein the tertiary dimethylamines are selected from the group consisting of dimethylalkylamines, alkylamidoalkyldimethylamines, other substituted dimethylalkylamines and mixtures thereof.

8. A composition according to claim 1 wherein the amount of tertiary dimethylamines used is in the range of from 1 to 50% by weight.
9. A composition according to claim 1 wherein the amount of tertiary dimethylamines used is in the range of from 10 to 25% by weight.
- 5 10. A composition according to claim 1 wherein the essentially non-aqueous polar solvents having low volatility are selected from group consisting of butane-1,3-diol, hexylene glycol or dipropylene glycol monomethyl ether.
11. A composition according to claim 1 wherein the amount of essentially non-aqueous polar solvent having low volatility is in the range of from 0.2 to 5% by weight.
- 10 12. A composition according to claim 1 wherein the additional solvent is selected from the group consisting of mono and di-glycerides of fat forming fatty acids, glycerol monooleate, glycerol dioleate, partial fatty acid esters of sorbitol anhydrides, sorbitan monooleate, sorbitan monolaurate, partial fatty acid esters of other polyols, pentaerythritol, polyglycerol, sugar pentitols and their anhydrides, sugar hexitols and their anhydrides, lecithin, low mole nonionic ethoxylates with alkyl or arylalkyl of 12 to 21 carbon atoms and 2 to 9 moles ethylene oxide adducted, and mixtures thereof.
- 15 13. A composition according to claim 1 wherein the amount of additional solvent is not in excess of 50% by weight.
- 20 14. A composition according to claim 13 wherein the amount of additional solvent is in the range of from 0.4 to 40% by weight.
15. A composition according to claim 1 wherein the lipophilic carrier is selected from the group consisting of petroleum fractions, vegetable oils, synthetic triglycerides, alkyl esters of fatty acids, fatty alcohols, guerbet alcohols or any mixture thereof.
- 25 16. A composition according to claim 15 wherein the lipophilic carrier is selected from the group consisting of aliphatic paraffinic light distillates or vegetable oils and their derivatives.
17. A composition according to claim 1 wherein the amount of lipophilic carrier is not in excess of 95% by weight.

18. A composition according to claim 1 further comprising one or more pesticides which are compatible with the lipophilic nature of the herbicide composition.
19. A composition according to claim 18 wherein the pesticides are selected from the group consisting of herbicides, fungicides, insecticides and mixtures thereof.
- 5 20. A composition according to claim 18 wherein the pesticide is 2,4-D.
21. A composition according to claim 1 further comprising other available adjuvant components.
- 10 22. A composition according to claim 21 wherein the other available adjuvant components are selected from the group consisting of plant nutrients, spray drift retardants, stickers, viscosity modifiers, spreaders and mixtures thereof.
23. A concentrated essentially non-aqueous homogeneous liquid herbicide composition comprising:
 - (a) a lipophilic solvent soluble complex comprising the reaction product of:
 - (i) not in excess of about 35% by weight of one or more lipophobic herbicides having an acidic moiety; and
 - (ii) not in excess of about 99% by weight of one or more tertiary dimethylamines of the structure $(CH_3)_2N-R$ wherein R contains an alkyl group of at least 8 carbon atoms and may contain other chemical moieties and wherein there is at least one mole equivalent of such amine to each mole of lipophobic herbicide; and
 - (b) not in excess of about 60% by weight of one or more essentially non-aqueous polar solvents having low volatility.
24. A concentrated composition according to claim 23 further comprising not in excess of 90% by weight of one or more essentially additional solvents selected from the group consisting of low to medium HLB surfactants.
25. A method for improving rainfastness of a lipophobic herbicide comprising the step of formulating the lipophobic herbicide in an essentially non-aqueous composition comprising:
 - (a) a lipophilic solvent soluble complex comprising the reaction product of:

- (i) not in excess of about 35% by weight of one or more lipophobic herbicides having an acidic moiety; and
 - (ii) not in excess of about 99% by weight of one or more tertiary dimethylamines of the structure $(CH_3)_2N-R$ wherein R contains an alkyl group of at least 8 carbon atoms and may contain other chemical moieties and wherein there is at least one mole equivalent of such amine to each mole of lipophobic herbicide;
- 5
- (b) not in excess of about 60% by weight of one or more essentially non-aqueous polar solvents having low volatility;
- 10
- (c) not in excess of about 90% by weight of one or more additional solvents selected from the group consisting of low to medium HLB surfactants; and
 - (d) not in excess of about 99% by weight of one or more lipophilic carriers.
26. A method for treating weeds comprising the step of applying to the weeds an essentially non-aqueous sprayable herbicide composition comprising:
- 15
- (a) a lipophilic solvent soluble complex comprising the reaction product of:
 - (i) not in excess of about 35% by weight of one or more lipophobic herbicides having an acidic moiety; and
 - (ii) not in excess of about 99% by weight of one or more tertiary dimethylamines of the structure $(CH_3)_2N-R$ wherein R contains an alkyl group of at least 8 carbon atoms and may contain other chemical moieties and wherein there is at least one mole equivalent of such amine to each mole of lipophobic herbicide;
- 20
- (b) not in excess of about 60% by weight of one or more essentially non-aqueous polar solvents having low volatility;
- 25
- (c) not in excess of about 90% by weight of one or more additional solvents selected from the group consisting of low to medium HLB surfactants; and
 - (d) not in excess of about 99% by weight of one or more lipophilic carriers.

27. A method for preparing an essentially non-aqueous sprayable herbicide composition comprising the steps of

(a) combining the following reagents:

- (i) not in excess of about 35% by weight of one or more lipophobic herbicides having an acidic moiety; and
- (ii) not in excess of about 99% by weight of one or more tertiary dimethylamines of the structure $(CH_3)_2N-R$ wherein R contains an alkyl group of at least 8 carbon atoms and may contain other chemical moieties and wherein there is at least one mole equivalent of such amine to each mole of lipophobic herbicide; and
- (iii) not in excess of about 60% by weight of one or more essentially non-aqueous polar solvents having low volatility; and

(b) combining the mixture formed in (a) with not in excess of about 90% by weight one or more additional solvents selected from the group consisting of low to medium HLB surfactants and not in excess of about 99% by weight one or more lipophilic carriers.

28. The method according to claim 27 wherein the reagents in step (a) are combined with heating and/or stirring.

29. The method according to claim 27 wherein the combining in step (b) comprises stirring the mixture whilst warm.

30. An essentially non-aqueous homogeneous liquid herbicide composition comprising:

(a) a lipophilic solvent soluble complex comprising the reaction product of:

- (i) not in excess of about 35% by weight of one or more lipophobic herbicides having an acidic moiety; and
- (ii) not in excess of about 99% by weight of one or more tertiary dimethylamines of the structure $(CH_3)_2N-R$ wherein R contains an alkyl group of at least 8 carbon atoms and may contain other chemical moieties and wherein there is at least one mole equivalent of such amine to each mole of lipophobic herbicide; and

- (b) not in excess of about 60% by weight of one or more essentially non-aqueous polar solvents which assist the formation of the lipophilic solvent soluble complex, wherein the complex is formed in the presence of the essentially non-aqueous polar solvent but the essentially non-aqueous polar solvent may be removed after formation of the complex if desired.
- 5
31. An essentially non-aqueous homogeneous liquid herbicide composition comprising:
- (a) a lipophilic solvent soluble complex comprising the reaction product of:
- (i) not in excess of about 35% by weight of one or more lipophobic herbicides having an acidic moiety; and
- 10 (ii) not in excess of about 99% by weight of one or more tertiary dimethylamines of the structure $(CH_3)_2N-R$ wherein R contains an alkyl group of at least 8 carbon atoms and may contain other chemical moieties and wherein there is at least one mole equivalent of such amine to each mole of lipophobic herbicide;
- 15 (b) not in excess of about 90% by weight of one or more additional solvents selected from the group consisting of low to medium HLB surfactants; and
- (c) not in excess of about 99% by weight of one or more lipophilic carriers.
32. An essentially non-aqueous homogeneous liquid herbicide composition comprising:
- (a) a lipophilic solvent soluble complex comprising the reaction product of:
- 20 (i) not in excess of about 35% by weight of one or more lipophobic herbicides having an acidic moiety; and
- (ii) not in excess of about 99% by weight of one or more tertiary dimethylamines of the structure $(CH_3)_2N-R$ wherein R contains an alkyl group of at least 8 carbon atoms and may contain other chemical moieties, wherein there is less than one mole equivalent of such amine to each mole of lipophobic herbicide;
- 25 (iii) not in excess of about 20% by weight of one or more hydrophilic amines;
- wherein the total mole equivalents of the amines in (ii) and (iii) is at least equivalent to the moles of lipophobic herbicide;
- 30

40

- (b) not in excess of about 60% by weight of one or more essentially non-aqueous polar solvents;
 - (c) not in excess of about 90% by weight of one or more additional solvents selected from the group consisting of low to medium HLB surfactants; and
 - 5 (d) not in excess of about 99% by weight of one or more lipophilic carriers.
33. An essentially non-aqueous homogeneous liquid herbicide composition comprising:
- (a) a lipophilic solvent soluble complex comprising the reaction product of:
 - (i) not in excess of about 25% by weight of glyphosate; and
 - (ii) not in excess of about 99% by weight of one or more tertiary dimethylamines of the structure $(CH_3)_2N-R$ wherein R contains an alkyl group of at least 8 carbon atoms and may contain other chemical moieties and wherein there is at least one mole equivalent of such amine to each mole of lipophobic herbicide;
 - (b) not in excess of about 60% by weight of one or more essentially non-aqueous polar solvents selected from 1,3-butanediol, hexylene glycol and mixtures thereof;
 - (c) not in excess of about 90% by weight of one or more additional solvents selected from the group consisting of low to medium HLB surfactants; and
 - (d) not in excess of about 99% by weight of one or more lipophilic carriers selected from the group consisting of aliphatic paraffinic light distillates or vegetable oils and their derivatives.

INTERNATIONAL SEARCH REPORT

International application No. PCT/AU01/01310
--

A. CLASSIFICATION OF SUBJECT MATTER		
Int. Cl. ⁷ : A01N 57/20, 25/02, 25/30		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) DERWENT WPI, JAPIO, CA, KEYWORDS: GLYPHOSATE, GLUFOSINATE, BILANFOS, NORAM, DIMETHYLAMINE, DIMETHYLCOCOAMINE, KENAMINE, GENAMINE, NON AQUEOUS		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,Y	US 4154596 A (GEORGE et al) 15 May 1979 Columns 1-3, Claim 2	1-33
Y	AU 200021541 A (MONSANTO) 13 June 2000 p3 lines 12-25, p 15 lines12-23,Table 4, claims	1-33
Y	AU 77400/94 A (MONSANTO) 11 May 1995 p42-43, claims	1-33
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "B" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed		"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family
Date of the actual completion of the international search 12 November 2001		Date of mailing of the international search report 19 NOV 2001
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaaustralia.gov.au Facsimile No. (02) 6285 3929		Authorized officer ROSS OSBORNE Telephone No : (02) 6283 2404

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU01/01310

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,Y	AU 200042761 A (VICTORIAN CHEMICALS INTERNATIONAL) 21 November 2000 Claims	1-33
A	WO 94/19941 A (KVK AGRO) 15 September 1994 Whole document	

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/AU01/01310

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
US	4154596	AU	29880/77	BR	7707244	CA	1101876
		DE	2749292	ES	463861	FR	2370047
		GB	1538502	IT	1088624	JP	53059096
		NZ	185451	ZA	7706143		
AU	200021541	WO	00/30452	US	6299755	DE	19757888
AU	77400/94	AU	77424/94				
AU	200042761	WO	00/67573				
WO	94/19941	AU	62568/98	DK	1117/93	EP	688165
		US	5795847	CA	2157526		
END OF ANNEX							